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IMPROVED ANODES FOR LIQUID HYDROCARBON FUEL CELL.(U)
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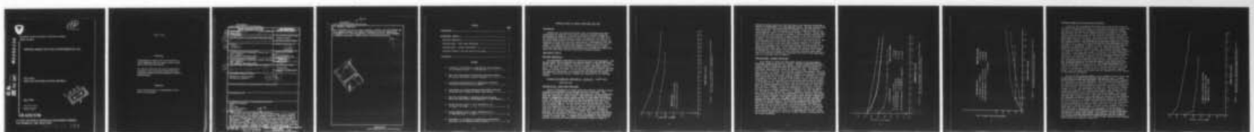

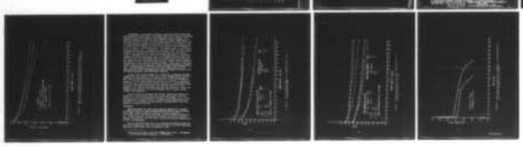

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RESEARCH AND DEVELOPMENT TECHNICAL REPORT

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IMPROVED ANODES FOR LIQUID HYDROCARBON FUEL CELL

John Perry
Electronics Technology & Devices Laboratory

April 1978

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Low power fuel cells operating on liquid hydrocarbons, such as methanol and ethylene glycol, have received renewed attention. The current state-of-the-art of anodes used in liquid hydrocarbon fuel cells operating at ambient temperatures of 22°C consist of platinum and palladium catalyst loadings of approximately 10 mg/cm². The cost and quantity of these noble metals required for anode electrode fabrication are high. Investigations conducted to reduce the noble metal catalyst loadings have lead to the development of an electrode consisting of graphite, platinum (2.4 mg/cm²), and anodic lead dioxide. over

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20. ABSTRACT - Continued.

Cells fabricated with the new anode (graphite, platinum, and lead dioxide) and silver amalgam cathodes were capable of operating at current densities of 20 mA/cm² at 0.60 V when charged with an anolyte solution of either methanol in potassium hydroxide or ethylene glycol in potassium hydroxide.

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FIGURES

IMPROVED ANODES FOR LIQUID HYDROCARBON FUEL CELL

INTRODUCTION

Methanol-air and ethylene glycol-air fuel cell batteries have been investigated for potential use as power sources in military equipments. Electrochemical oxidation of methanol and ethylene glycol in single cells has demonstrated good performance; however, the high cost and quantity of the noble metals required for anode electrode fabrication have limited the acceptance of these fuel cells as a power source. Investigations have been conducted to reduce the noble metal catalyst loadings on the anode electrodes. This report discusses the preparation and evaluation of anode electrodes fabricated with non-noble metals only and anode electrodes fabricated with noble metal catalysts coupled with non-noble metals.

EXPERIMENTAL RESULTS

Electrode Fabrication

The experimental electrodes are fabricated in the following manner. The process begins with wet blending the catalyst powders in the desired weight percent ratio. After blending, a solution of teflon was added to the mix and the mixture heated while stirring until the catalyst coagulated forming a paste. The paste was rolled onto a silver screen current collector, and then dried for two hours at 100°C. A hand rolling technique was used in applying the catalyst to the screen, which resulted in some variation in catalyst loadings. Noble metal catalyst loadings were determined by the following formula:

$$\frac{\%\text{ noble in original mix (electrode wt - screen wt)}}{\text{electrode area}} = \text{mg/cm}^2\text{ noble}$$

Platinum Black - Lead Powder Electrodes

Initial investigations to reduce noble metal catalyst loadings on anode electrodes were conducted using platinum black and lead powder. The platinum (Pt) black and lead (Pb) powder were mixed with teflon as described above and rolled onto a silver screen. Some difficulty was experienced in getting a homogeneous catalyst paste mix with the lead powder and platinum black. The lead powder being heavier than the platinum would settle to the bottom of the mixing vessel during the paste preparation and when rolled onto the screen support, the lead formed a sheet and shielded much of the active platinum catalyst. It was felt that the malleable properties of the lead were responsible for the erratic performance obtained from electrodes fabricated with lead powder. Experimental electrodes were evaluated in half cell test fixtures containing 3 M ethylene glycol + 11 M potassium hydroxide, at room ambient temperature of 22°C. The electrodes were tested by driving the electrode with a power supply and measuring the polarization voltages at various loads. A comparison of performances of the palladium-platinum electrodes and lead-platinum electrodes is shown in Figure 1.

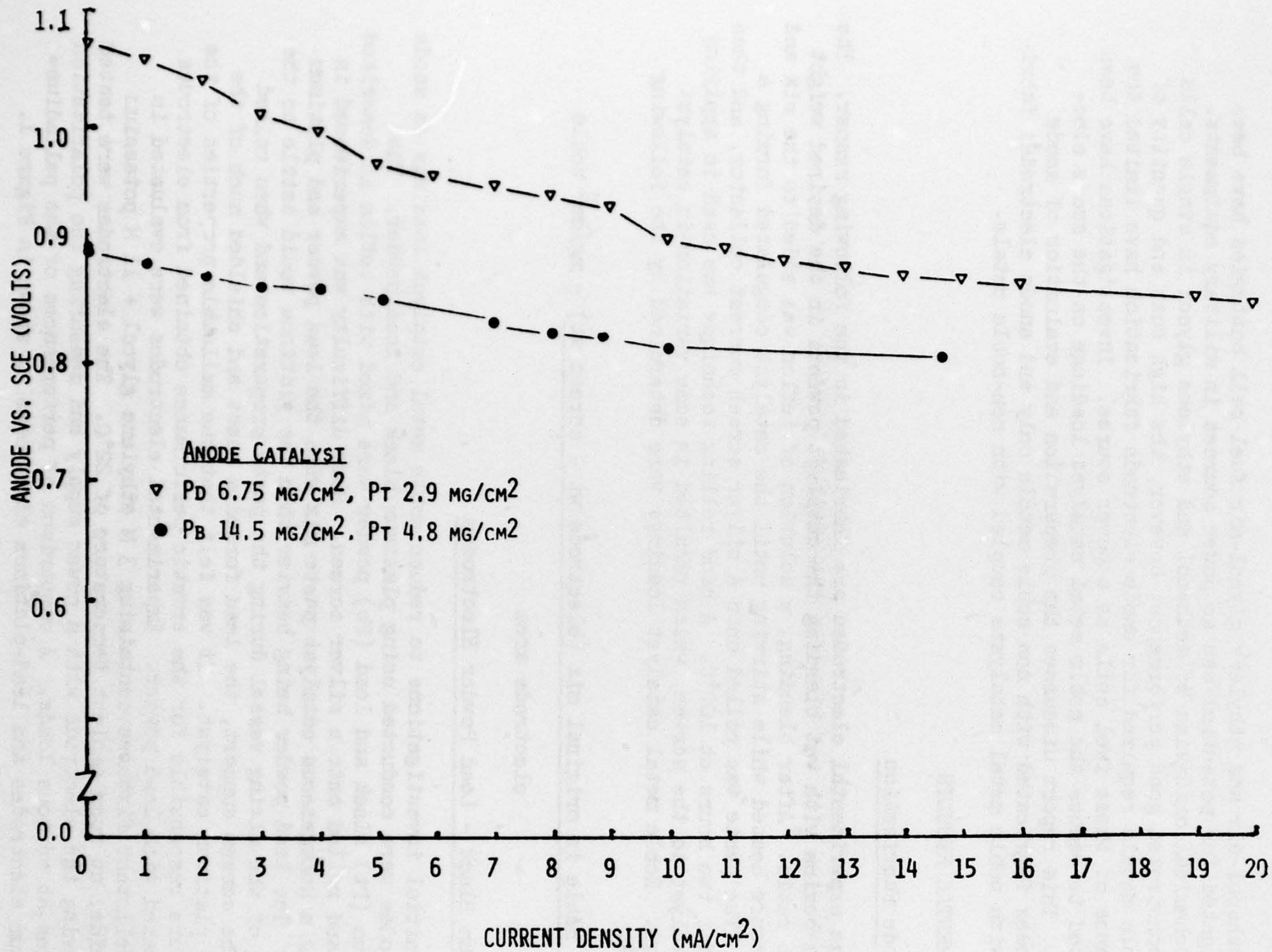

Figure 1. Comparison of Performance of Experimental Anode Catalysts in 3 M Ethylene Glycol + 6 M KOH Anolytes

Saturated calomel electrodes (SCE) were used as the reference electrodes to measure the performance of the experimental anodes. The open circuit potentials of the Pb-Pt electrodes were approximately 150 mV lower than the Pd-Pt electrodes. The lead appeared to have had a negative effect on the electrochemical activity of the electrode catalyst. However, initial tests showed that the load polarization voltage of the electrodes containing lead was less than the polarization voltage obtained for the Pd-Pt electrode at 10 mA/cm^2. The Pd-Pt electrode polarized 0.166 V from the open circuit potential and the Pb-Pt electrode polarized 0.078 V from open circuit. The Pd-Pt electrode had a total noble metal catalyst loading of 9.65 mg/cm^2 while the Pb-Pt had a total noble metal catalyst loading of 4.8 mg/cm^2. These tests indicated that the lead powder limited the polarization of the electrode while under load. Other electrodes with various combinations of platinum black to lead powder were fabricated and evaluated in an attempt to increase the load voltage of anode electrodes containing lead powder. None of the catalyst combinations containing lead powder showed improvement over the electrodes shown in Figure 1.

Platinum Black - Graphite Electrodes

In an effort to reduce the lead powder content in the experimental electrodes, graphite was used as a filler. Catalyst preparation and electrode fabrication techniques were similar to those described previously. A graphite powder-platinum electrode was fabricated first to determine the performance characteristics before the addition of lead. The catalyst paste mix used to fabricate the electrodes contained 84% graphite, 16% noble metal catalyst, and teflon. Half cell performances of electrodes containing graphite and reduced noble metal catalyst loadings were compared to an electrode with higher noble catalyst loadings (Figure 2). The electrodes with the graphite filler and 3.4 mg/cm^2 of noble metal catalyst had open circuit voltages equal to the electrode with the high noble metal catalyst loading of 12 mg/cm^2 (Pt-Pd). Load voltages of the electrodes with low noble metal catalyst loadings averaged 60 mV lower than the electrodes with high noble metal catalyst loadings. The anolyte solution was 3 M glycol + 6 M KOH. The lower curve in Figure 2 shows the performance of an electrode catalyst consisting of 14.5 mg/cm^2 of graphite, 3.4 mg/cm^2 of Pt, and 5 mg/cm^2 of Pb. The addition of lead powder to the Pt-graphite electrode lowered the open circuit voltage 200 mV. The performance of this electrode was similar to the previous electrode with the higher noble metal catalyst loading plus lead, as shown in Figure 1, thus again showing that the anode catalyst containing the lead powder has a negative effect on the voltage performance. Although the voltage levels of the electrodes containing the lead powder were low, as shown in Figures 1 and 2, the polarization relationship of electrodes with noble metal catalyst only and electrodes with lead powder added indicate that lead reduces the polarization effects of the electrode when under load, as shown in Figure 3. Polarization effects of the electrodes containing lead powder level off at approximately 3 mA/cm^2, whereas the electrodes containing no lead show a steady increase in polarization as the current increases.

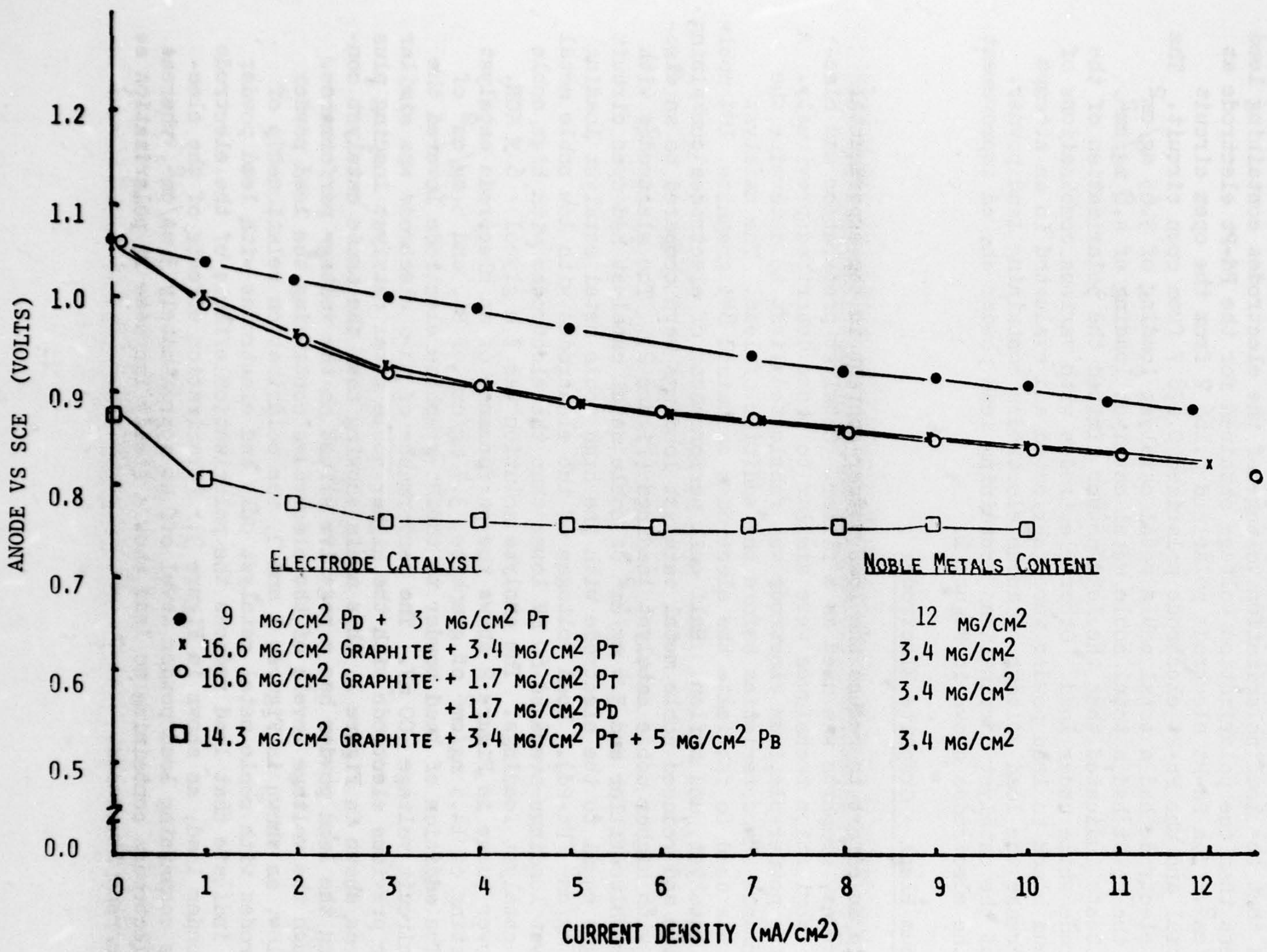

Figure 2. Half Cell Performances of Electrodes Containing Graphite and Various Noble Metal Catalyst Loadings

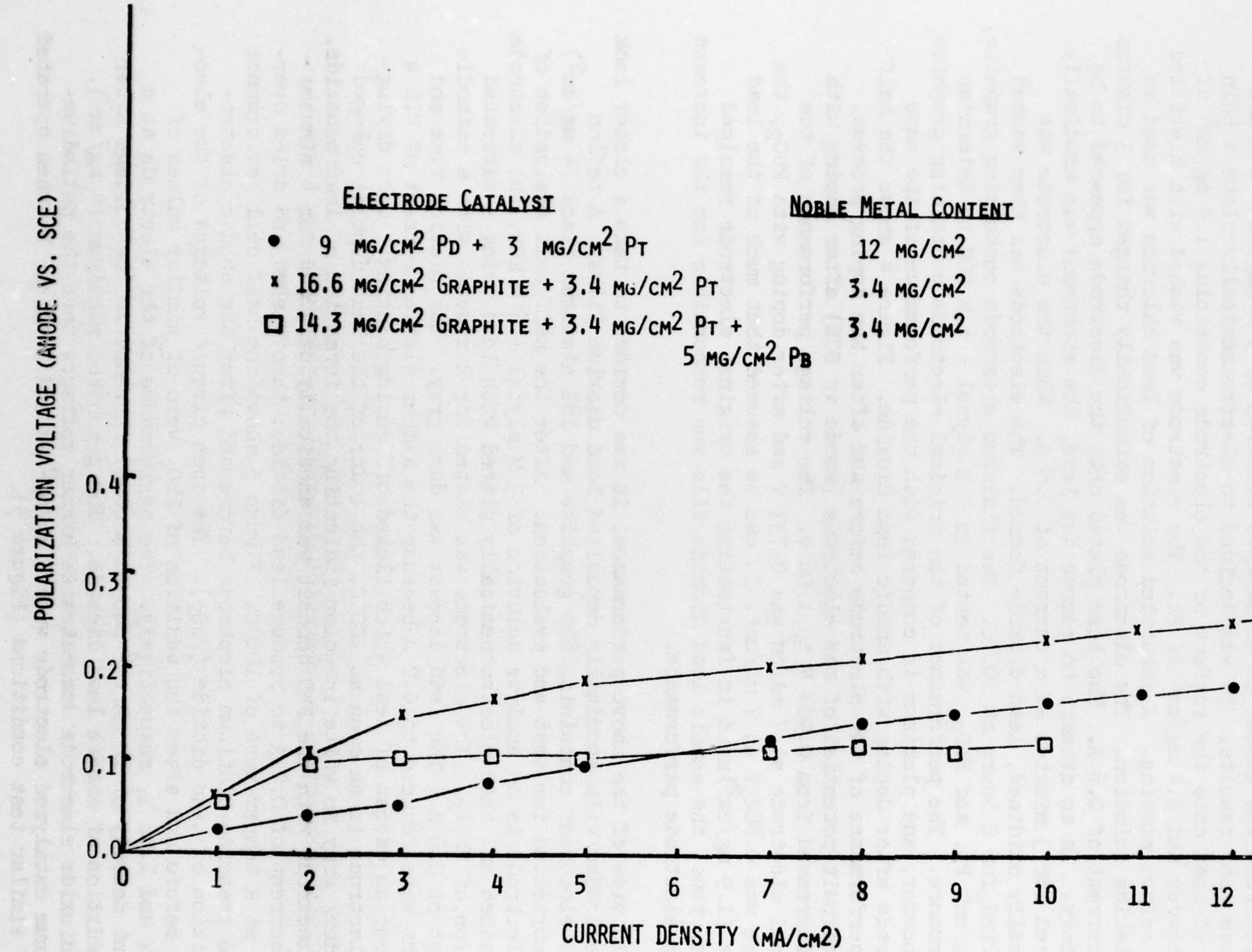

Figure 3. Polarization Characteristics of Electrodes Fabricated With Noble Metal Catalyst and Graphite

Platinum, Graphite, and Lead Dioxide Electrodes

In view of the encouraging load polarization data obtained from the electrodes containing lead powder, the lead powder content was reduced from 5 mg/cm^2 to 1.9 mg/cm^2 in an attempt to increase the operating voltage. The electrode was tested in an anolyte solution of 3 M glycol + 6 M KOH and gave poor results. It was decided to electrochemically plate a thin layer of lead onto the surface of the electrode containing 1.9 mg/cm^2 of lead powder and 3.4 mg/cm^2 of Pt. The electrode was washed with distilled water before plating. A saturated solution of lead chloride was used as the plating solution. The electrode was cathodically charged for 3 minutes at a current of 0.6 A. The lead plated onto the electrode appeared to be too heavy. In an attempt to remove the lead, the electrode was anodically oxidized for 3 minutes at a current of 0.6 A. When the electrode was anodically oxidized, lead dioxide formed. The electrode was then washed and dried for 2 hours at 100°C. The finished electrode containing graphite, 3.4 mg/cm^2 Pt, and PbO_2, was tested in 3 M glycol + 6 M KOH to determine performance. The performance of the original electrode containing graphite, lead powder, and platinum is compared with the performance of the same electrode after doping with anodic lead dioxide. Figure 4 shows the half cell performance of the electrode before and after the doping process. Open circuit potential of the electrode (anode vs SCE) after doping with PbO_2 increased from 0.904 V to 1.06 V. The voltage performance of the original electrode at 7 mA/cm^2 was 0.737 V and after doping with PbO_2, the voltage was 0.882 V at 7 mA/cm^2. It can be assumed that much of the lead powder (1.9 mg/cm^2) used in fabricating the original electrode remained intact; thus, the anodic lead dioxide film was responsible for the increase in the electrode performance.

In view of the above performance, it was decided to take a closer look at electrodes with anodically deposited lead dioxide films. A teflon bonded electrode containing 82% graphite and 18% platinum black (4 mg/cm^2) was fabricated for test and evaluation. After the half cell evaluation of the electrode in an anolyte solution of 3 M glycol + 6 M KOH, the electrode was washed and then electrochemically plated with lead using a saturated solution of $PbCl_2$. The electrode was plated for 2 minutes with a cathodic current of 0.6 A. The lead deposit was dark gray. The plating time and current were reduced to 0.2 A because the higher plating current of 0.6 A produced an excess of lead which flaked off during plating. Upon drying the electrode in an oven at 100°C, the color of the lead deposit changed from dark gray to white in color indicating the formation of lead monoxide. The electrode with the PbO deposit was anodically oxidized for 4 minutes at a current of 0.2 A to produce lead dioxide; then washed and dried overnight at a temperature of 100°C. Figure 5 shows the half cell performance of the graphite-platinum electrode before and after the anodic electrodeposition of lead dioxide (PbO_2). The open circuit voltages of the electrode before and after the addition of PbO_2 were of similar values of 1.07 V and 1.06 V, respectively. The performance of the electrode at a current density of 10 mA/cm^2 showed a 60 mV increase in the voltage after the addition of anodic lead dioxide. The graphite, platinum (4 mg/cm^2), lead dioxide electrode demonstrates higher voltages than the palladium-platinum catalyzed electrode with 7 mg/cm^2 Pd and 3 mg/cm^2 Pt when operated under similar test conditions (Figure 5).

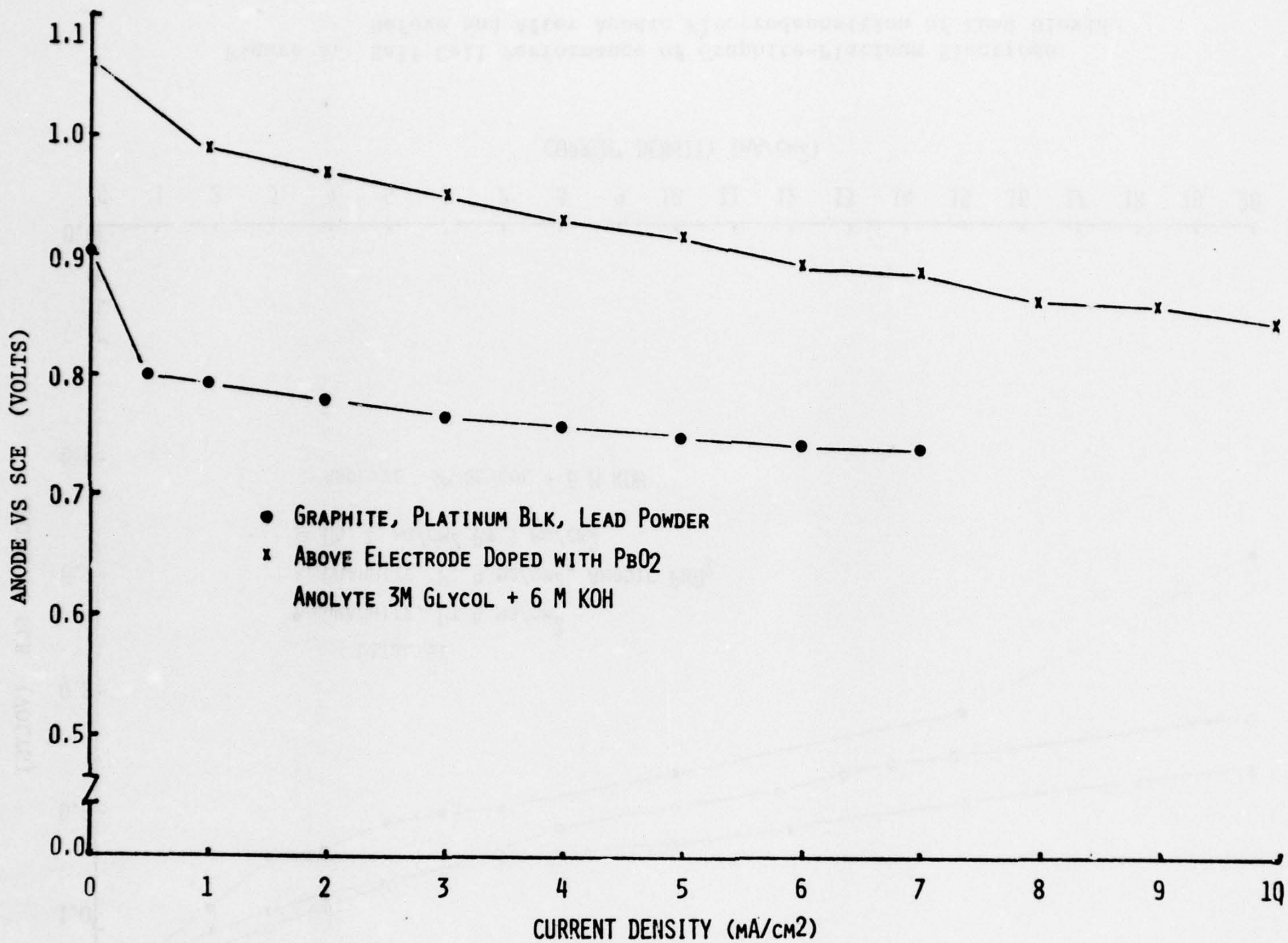

Figure 4. Performance of a Platinum-Graphite-Lead Powder Electrode Before and After Doping With Anodic Lead Dioxide

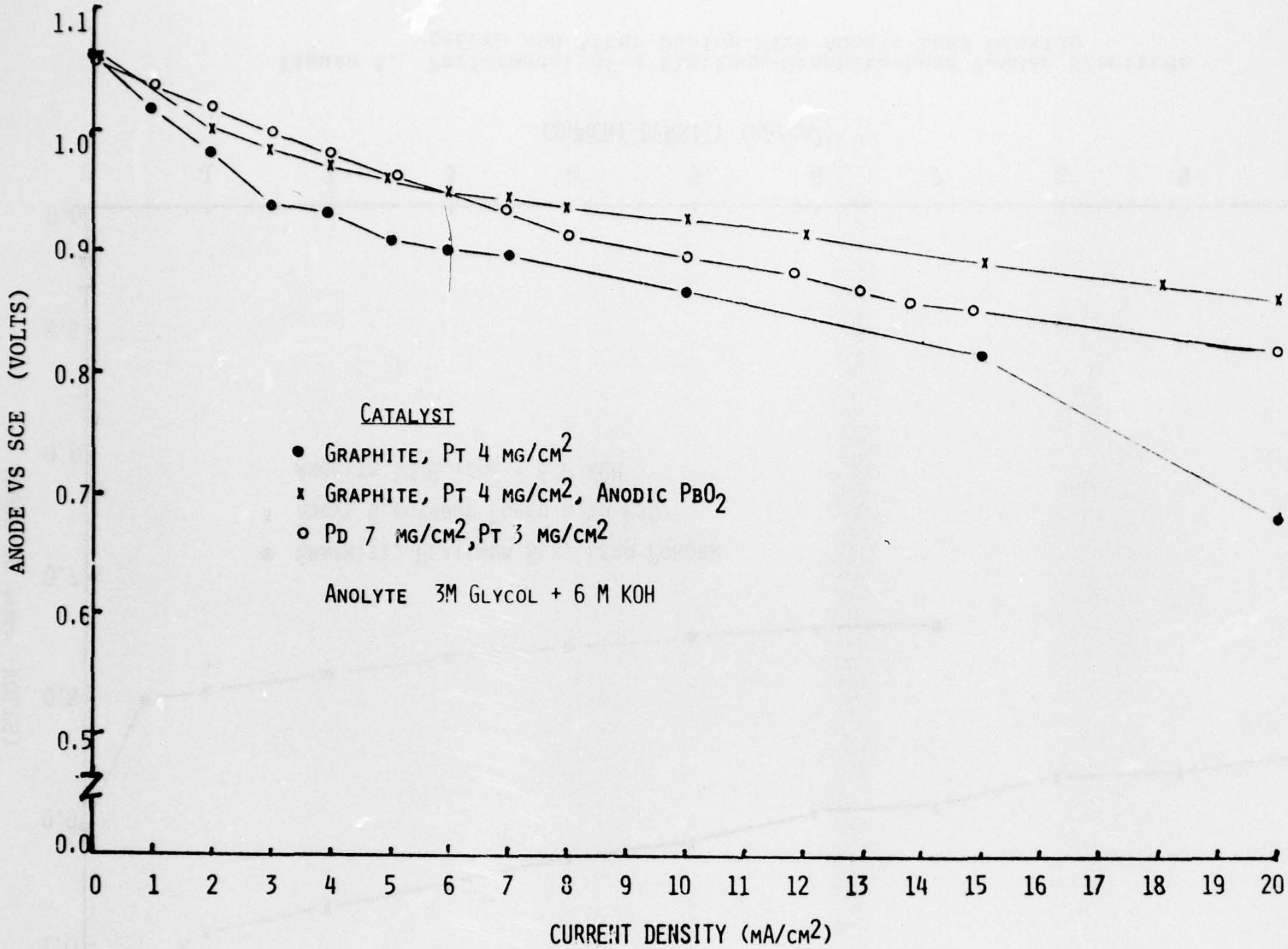

Figure 5. Half Cell Performance of Graphite-Platinum Electrode Before and After Anodic Electrodeposition of Lead Dioxide

Performance of the graphite, platinum, lead dioxide anode electrodes was evaluated in single cells. The single cells were of the bi-cell design, complete with two air breathing silver amalgam catalyst cathodes. The anode was centrally located in a cell frame with exterior dimensions of 5.08 cm x 8.9 cm x 0.95 cm. The active anode area (both sides) was 62 cm^2. The anode catalyst contained 11.2 mg/cm^2 of graphite, 2.45 mg/cm^2 Pt, and 0.3 mg/cm^2 of lead dioxide. Current density curves of cells operating on air - 6 M CH_3OH + 11 M KOH and on air - 3 M ethylene glycol + 6 M KOH are shown in Figures 6 and 7, respectively. The upper curves in these figures represent the half cell performance of the anode vs SCE. The lower curves represent the performance of single cells fabricated with the anodes listed. Performance of the cell with the anode containing a low platinum loading and anodic lead dioxide (Cell A) is compared with two other cells (Cells B and C) both containing anodes with higher noble metal catalysts. All single cells were fabricated with the silver amalgam catalyst cathodes. The anodes for Cells A and B were made in-house. Cell C was a single cell removed from a 6-cell methanol-air lantern battery (experimental), manufactured by Energy Research Corporation under Government Contract DAAB07-76-C-1681. The performance of the cell with the low noble metal catalyst loading plus PbO_2 gave approximately the same performance as the cell with the anode containing a high noble metal catalyst.

Figure 8 shows the performance of a single cell containing the experimental anode (Pt, graphite, PbO_2) and a silver amalgam catalyst cathode, operating on anolyte mixtures of ethylene glycol in KOH and methanol in KOH. The cell was first operated with 20 cc of 3 M glycol + 6 M KOH at a constant 0.5 A (10 mA/cm^2) load to a cutoff of 0.5 V. At the completion of the test with glycol anolyte solution, the cell was drained and flushed with boric acid solution and water, then refilled with 20 cc of 6 M methanol + 11 M KOH and tested under the same test condition. These tests demonstrate the capability of the experimental anode to operate under constant load conditions.

Previous studies on methanol-air batteries showed that methanol-air batteries, in the activated state, have a poor shelf life.[1] The poor shelf life is due to the evaporation losses of the methanol fuel. Cells activated with 3 M ethylene glycol + 6 M KOH also had limited shelf life. The glycol in the presence of KOH undergoes polymerization after long periods of storage in the cell.

CONCLUSIONS

Anode electrodes with noble metal catalyst loadings of 2.4 mg/cm^2 platinum and doped with anodic PbO_2 demonstrated current density performances equal to anodes containing high noble catalyst loadings of 12.7 mg/cm^2 Pt-Pd. The total noble metal catalyst loading was reduced by 81%. Further reduction of noble metal catalysts used on the anodes in methanol and glycol-air type fuel cells, operating at ambient temperatures of 22°C, are envisioned.

The poor activated shelf life of the methanol and ethylene glycol air fuel cells limits use of these low power fuel cells in military equipments operating intermittently over long periods of time.

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[1] John Perry & M. Klein, "Low Power Methanol Fuel Cells," Proceedings of 27th Power Sources Symposium, p. 178 (1976).

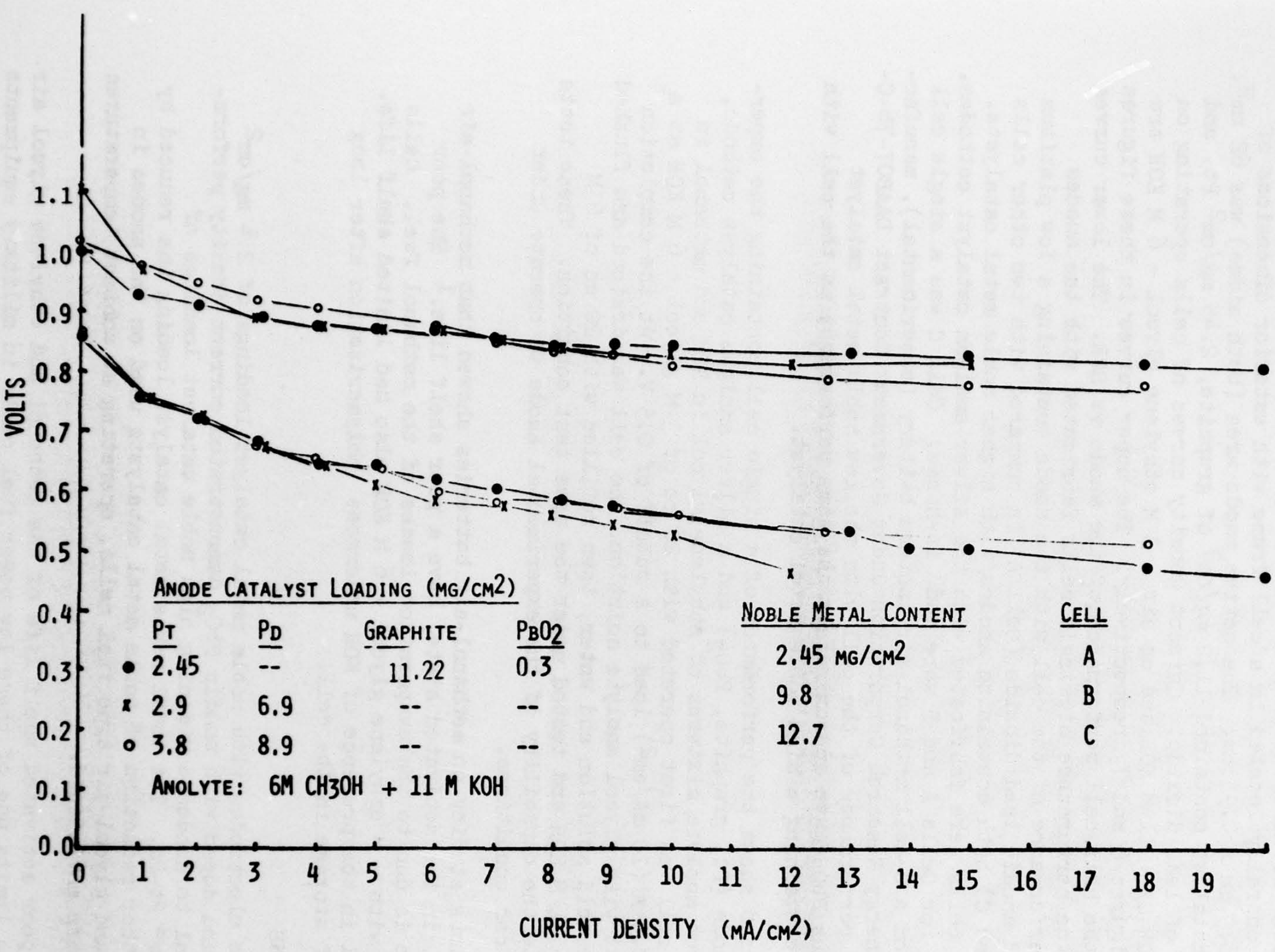

Figure 6. Current Density Curves of Cells Operating on Air - 6 M CH_3OH + 11 M KOH

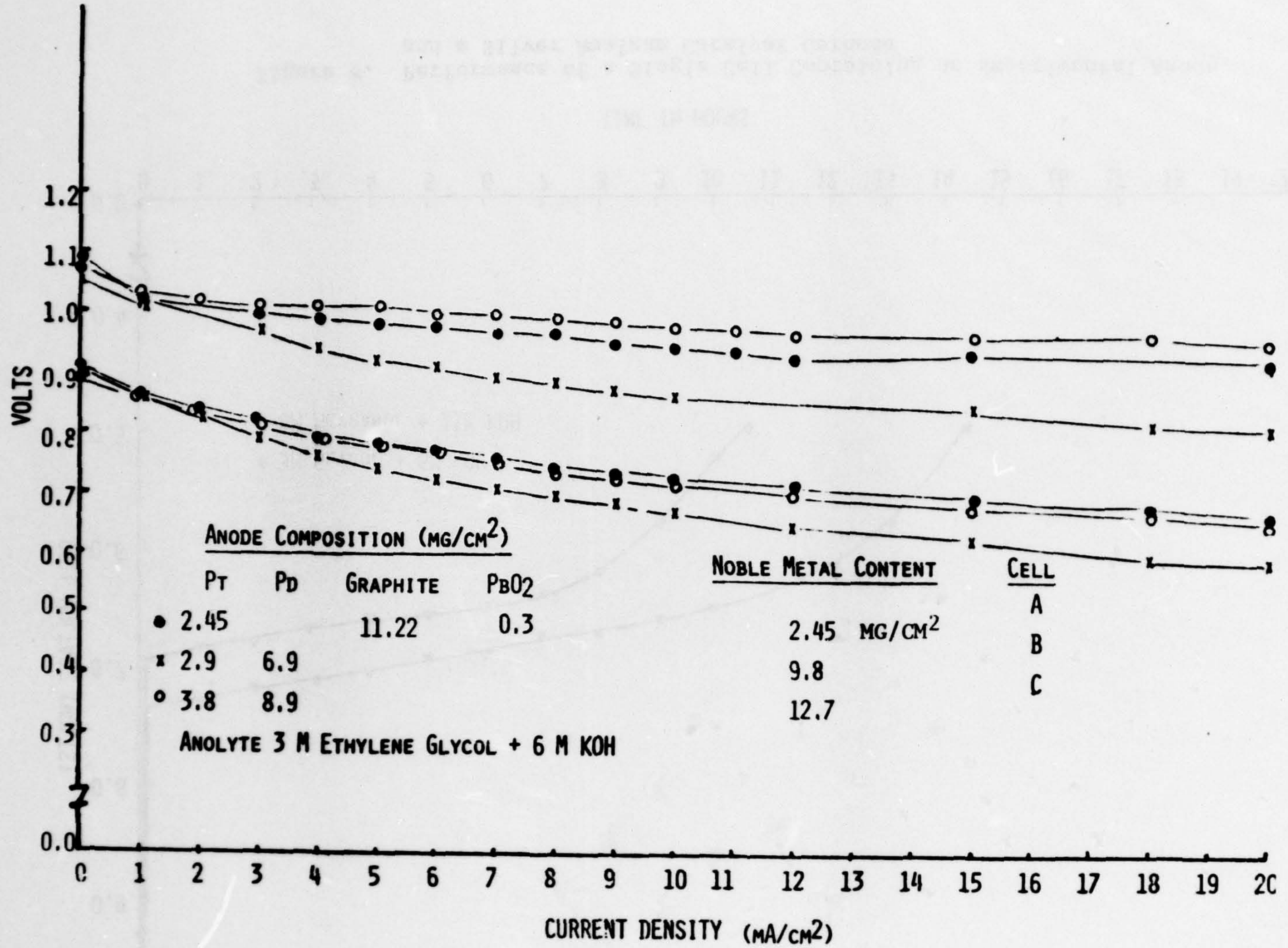

Figure 7. Current Density Curves of Cells Operating on Air - 3 M Ethylene Glycol + 6 M KOH

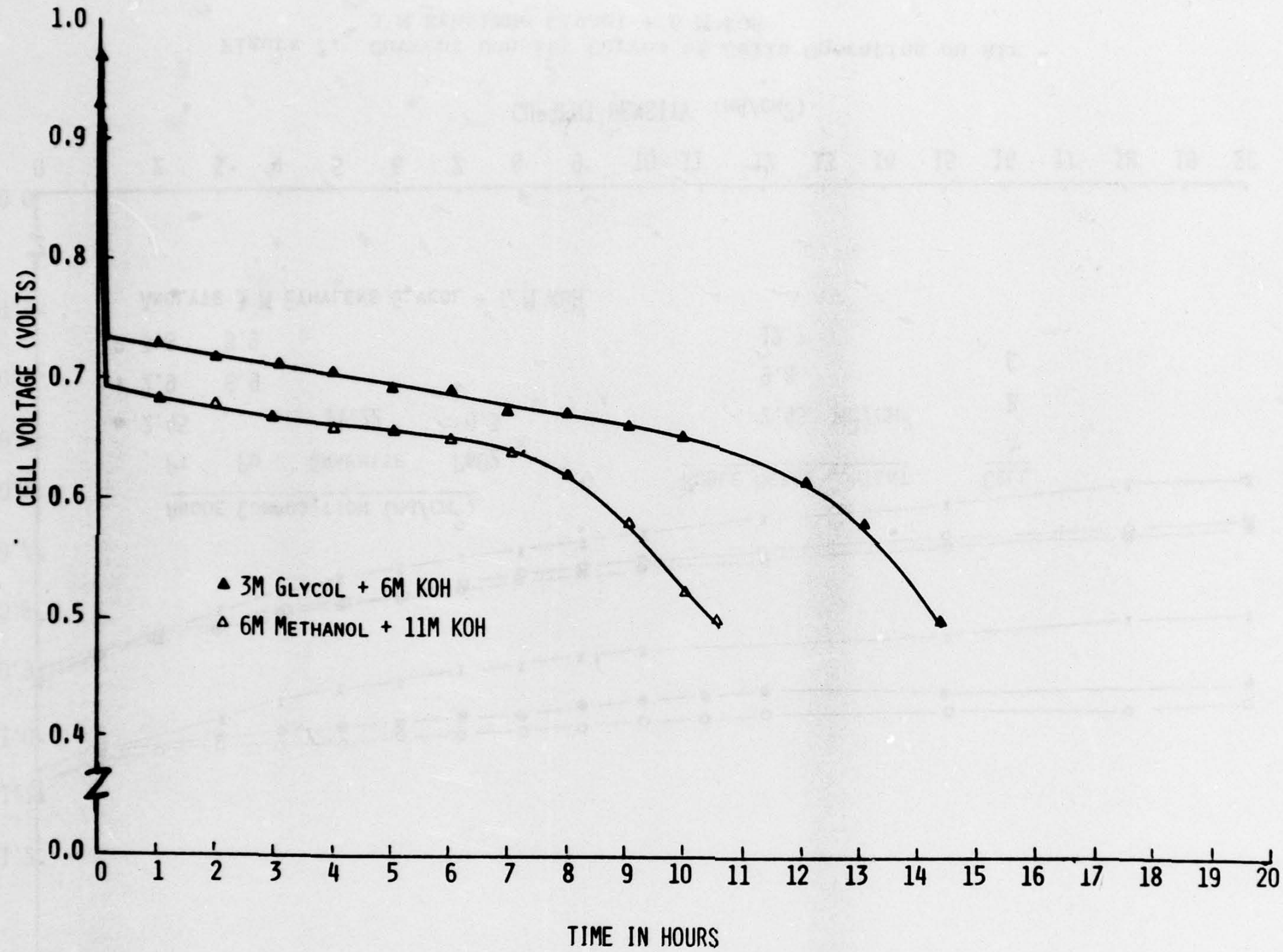

Figure 8. Performance of a Single Cell Containing an Experimental Anode and a Silver Amalgam Catalyst Cathode